Electron Spin Resonance Studies of Bis(η-cyclopentadienyl) Compounds of Molybdenum and Tungsten

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A series of cations of the general formula $[M(cp)_2(X)Y]^+$ (M = Mo or W; X and Y are equivalent to uninegative unidentate ligands; cp = η-cyclopentadienyl), have been produced by oxidation with chemical oxidants, by electrolysis, or by exchange reactions. The e.s.r. spectra of these paramagnetic species have been studied in solution and the $\langle g \rangle$ values and solution hyperfine coupling constants are discussed. Spectra of glasses of some of the cations are also presented.

THERE has been considerable interest in bis(η-cyclopentadienyl) compounds of the early transition metals since they show a wide ranging chemistry. A molecular-orbital (m.o.) description of the bonding in these compounds was originally put forward by Ballhausen and Dahl.[1] This accounted for the then known basic properties of the hydrides $[M(cp)_2H_n]$ (cp = η-C_5H_5; M = Ta, Mo, W, or Re). Structural studies by Alcock,[2] however, suggested an alternative bonding scheme. In the light of further structural studies on many bis(η-cyclopentadienyl) compounds, Green *et al.*[3] proposed a more flexible m.o. approach which reconciled the two theories with the experimentally determined molecular geometries and recent photoelectron spectroscopic data support this model.[4] E.s.r. studies have been made on compounds of Ti, V, Nb, and Ta [5-9] and the data have been discussed in relation to three different m.o. treatments,[6-8] primarily of vanadium compounds, but there is not a high degree of agreement between these calculations. Dias [10] described and assigned the electronic spectra of many compounds of the type $[M(cp)_2X_n]$, including some of molybdenum and tungsten discussed below.

In this study a variety of compounds of Mo^{IV} and W^{IV} have been prepared of the general formula $[M(cp)_2(X)Y]$ (X and Y are equivalent to uninegative unidentate ligands) and some compounds of Mo^{V} and W^{V} have been characterised. Here the e.s.r. spectra of the latter species are described together with those of cations formed by oxidation of the former species.

EXPERIMENTAL

The compounds were prepared as in earlier publications [11-15] except as described below. E.s.r. spectra were recorded on a JEOL *X*-band spectrometer at 100 MHz modulation frequency and were calibrated with 1,1-diphenyl-2-picrylhydrazyl and an aqueous n.m.r. field marker. Spectra of glasses were recorded in dimethyl sulphoxide at < -100 °C. The experimental work was carried out in the Inorganic Chemistry Laboratories, South Parks Road, Oxford.

Chemical Oxidation of $[M(cp)_2(X)Y]$.—Salts $[M(cp)_2(X)Y][PF_6]$ (Tables 1 and 2) were obtained by oxidation of $[M(cp)_2(X)Y]$ in an aqueous suspension or solution with nitric acid or hydrogen peroxide. A saturated solution of $[H_4N][PF_6]$ was quickly added to the resulting clear solution to precipitate the salt which was then recrystallised from liquid sulphur dioxide.

Electrolytic Oxidation of $[M(cp)_2(X)Y]$.—The electrolytic cell used for oxidation in the e.s.r. spectrometer cavity comprised an evacuable flat cell with a platinum-gauze anode and bright platinum cathode. The sample, $[M(cp)_2(X)Y]$ (10^{-3}—10^{-4} mol dm^{-3} in 1,2-dimethoxyethane (dme), acetone, or dimethyl sulphoxide) and supporting electrolyte, $[Bu^n{}_4N][ClO_4]$ (10^{-1} mol dm^{-3}), were electrolysed at a minimum applied voltage in the range 1—3 V. The first e.s.r. signal obtained was recorded and in most cases no other signals were observed up to a maximum of 4.5 V applied.

RESULTS

Oxidation by chemical oxidants of diamagnetic compounds $[M(cp)_2(X)Y]$ (M = Mo or W) in some cases led to paramagnetic cations which were isolated as salts of the $[PF_6]^-$ anion [equation (1)]. These species showed well resolved e.s.r. spectra in solution at ambient temperatures and the parameters from such spectra are shown in Tables 1 and 2.

$$[M(cp)_2(X)Y] \xrightarrow[(ii)\ [H_4N][PF_6]]{(i)\ \text{oxidation}} [M(cp)_2(X)Y][PF_6] \qquad (1)$$

Chemical oxidations of other products of the type $[M(cp)_2(X)Y]$ led to decomposition so that simple cationic species could not be isolated. However, it is very likely that the initial products of oxidation are cations $[M(cp)_2(X)Y]^+$, formed by electron transfer, which may then undergo subsequent decomposition reactions. In these cases *in situ* electrolytic oxidation in an e.s.r. spectrometer was carried out at a potential which was the minimum required to produce a paramagnetic species. Using this method it was possible to record e.s.r. spectra from a wider

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[1] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, 1961, **15**, 1333.

[2] N. W. Alcock, *J. Chem. Soc.* (*A*), 1967, 2001.

[3] J. C. Green, M. L. H. Green, and C. K. Prout, *J.C.S. Chem. Comm.*, 1972, 421.

[4] J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1975, 403.

[5] J. G. Kenworthy, J. Myatt, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 1020, 3428 and refs. therein.

[6] D. P. Bakalik and R. G. Hayes, *Inorg. Chem.*, 1972, **11**, 1732.

[7] C. P. Stewart and A. L. Porte, *J.C.S. Dalton*, 1973, 722.

[8] J. L. Petersen and L. F. Dahl, *J. Amer. Chem. Soc.*, 1974, **96**, 2248.

[9] I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Mauzer, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, 1974, **96**, 7374.

[10] A. R. Dias, *Rev. Port. Quim*, 1971, **13**, 222.

[11] R. L. Cooper and M. L. H. Green, *J. Chem. Soc.* (*A*), 1967, 1155.

[12] M. L. H. Green and W. E. Lindsell, *J. Chem. Soc.* (*A*), 1967, 1455.

[13] M. G. Harriss, M. L. H. Green, and W. E. Lindsell, *J. Chem. Soc.* (*A*), 1969, 1453.

[14] E. Gore, M. L. H. Green, M. G. Harriss, W. E. Lindsell, and H. Shaw, *J. Chem. Soc.* (*A*), 1969, 1981.

[15] M. L. H. Green and W. E. Lindsell, *J. Chem. Soc.* (*A*), 1969, 2150, 2215.

range of $[M(cp)_2(X)Y]$ compounds. The symmetrical signals obtained are assignable to a single species which on the basis of *g* values and the presence of appropriate hyperfine coupling must contain metal. Electrolytic oxidation gave identical spectra to those of the cations isolated from chemical oxidation and similarly the signals from other $[M(cp)_2(X)Y]$ compounds are assigned to the cations in Tables 1 and 2. The signals of these latter species were observed within a few minutes electrolysis above a threshold voltage in the range 1—3 V (secondary signals appeared in a few cases after prolonged electrolysis for 2—3 h). The paramagnetic species decayed slowly on cessation of the current and so are unstable, but reversal of the current caused a more rapid loss of spectrum.

TABLE 1

E.s.r. parameters of molybdenum cations in solution

Cation	$\langle g \rangle$	$10^4 \langle a \rangle$(Mo)/cm^{-1}	χ/a.u.	$10^4 \langle a \rangle$(X)/cm^{-1}
$[Mo(cp)_2(NHC_6H_4O)]^+$ [a]	1 9710 [b]			
$[Mo(cp)_2(O_2CCF_3)_2]^+$ [a]	1 9808 [b]	(+) 36.6 ± 0.5	−4.5	
$[Mo(cp)_2(O_2CPh)_2]^+$ [a]	1.9823 [b]	(+) 36.5 ± 0.5	−4.5	
$[Mo(cp)_2(NCS)_2]^+$ [a]	1.9853 [c]	(+) 33.0 ± 1.0	−4.1	
$[Mo(cp)_2(N_3)_2]^+$ [d]	1.9859 [c]	(+) 31.4 ± 0.5	−3.9	
$[Mo(cp)_2Cl_2]^+$ [d]	1.9988 [c]	(+) 34.5 ± 0.5	−4.4	3.1 ± 0.1 [e]
$[Mo(cp)_2(NHC_6H_4S)]^+$ [a]	2.0013 [b]			
$[Mo(cp)(C_6F_5)(\eta\text{-}C_5H_4{\cdot}C_6F_5)Cl]^+$ [d]	2.0054 [b] (2.0056) [c]	(+) 31.9 ± 0.5	−4.1	4.7 ± 0.2 [e]
$[Mo(cp)_2(tdt)]^+$ [d]	2.0089 [b] (2.0092) [c]	(+) 16.1 ± 0.5	−2.1	
$[Mo(cp)_2(Br)Cl]^+$ [d]	2.0258 [b] (2.0250) [c]	(+) 31 ± 3	−4.2	15 ± 0.5[f]
$[Mo(cp)_2Br_2]^+$ [d]	2.0535 [b]	(+) 31 ± 3	−4.3	15 ± 0.2 [f]

[a] Electrolytically produced. [b] In 1,2-dimethoxyethane (±0.001). [c] In dimethyl sulphoxide (±0.001). [d] Isolated as a salt. [e] ^{35}Cl–^{37}Cl. [f] ^{79}Br–^{81}Br.

TABLE 2

E.s.r. parameters of tungsten cations in solution

Cation	*g*	$10^4 \langle a \rangle$(W)/cm^{-1}	χ/a.u.	$10^4 \langle a \rangle$(X)/cm^{-1}
$[W(cp)_2(O_2CCF_3)_2]^+$ [a]	1.927 ± 0.003 [b]	(−) <58	<−11	
$[W(cp)_2(O_2CPh)]^+$ [a]	1.9303 [b]	(−) ⩽50	⩽−9.4	
$[W(cp)_2(N_3)_2]^+$ [c]	1.9416 [d]			
$[W(cp)_2(NCS)_2]^+$ [c]	1.9456 [e] (1.942 ± 0.003) [d]	(−) ⩽49	⩽−9.4	
$[W(cp)_2Cl(NCS)]^+$ [c]	1.9486 [d]	(−) 49 ± 3	−9.4	
$[W(cp)_2(O_2C_{14}H_8)]^+$ [a]	1.9544 [b]			
$[W(cp)_2Cl_2]^+$ [c]	1.9554 [b] (1.9544 [e])	(−) 47 ± 3	−9.2	
$[W(cp)_2(CN)(OEt)]^+$ [a]	1.9554 [b]	(−) 47 ± 3	−9.1	
$[W(cp)_2(NCS)(SCN)]^+$ [c]	1.9660 [e] (1.965 ± 0.003 [d])	(−) 43 ± 3	−8.3	
$[W(cp)_2(NHC_6H_4S)]^+$ [a]	1.9777 [b]	(−) ⩽42	⩽−8.3	
$[W(cp)(C_6F_5)(\eta\text{-}C_5H_4{\cdot}C_6F_5)Cl]^+$ [c]	1.9825 [b] (1.9824) [d]	(−) 54.2 ± 1	−10.9	6.3 ± 0.2
$[W(cp)_2(Br)Cl]^+$ [g]	1.985 ± 0.002 [g]			23 ± 1.5 [h]
$[W(cp)_2(tdt)]^+$ [c]	1.9944 [b] (1.9939) [d]	(−) 29 ± 2	−5.9	
$[W(cp)_2Br_2]^+$ [c]	2.0131 [e]	(−) 49 ± 3	−10.2	21.9 ± 0.2 [h]
$[W(cp)(C_6F_5)(\eta\text{-}C_5H_4{\cdot}C_6F_5)Br]^+$ [c]	2.0258 [b] (2.0253) [e]	(−) 48 ± 3	−10.0	30.8 ± 1 [h]

[a] Electrolytically produced. [b] In 1,2-dimethoxyethane (±0.001 unless otherwise stated). [c] Isolated as a salt and produced electrolytically. [d] In acetone (±0.001 unless otherwise stated). [e] In dimethyl sulphoxide (±0.001). [f] ^{35}Cl–^{37}Cl. [g] From exchange in concentrated HCl or HBr. [h] ^{79}Br–^{81}Br.

The cations $[M(cp)_2X_2]^+$ (M = Mo or W; X = Cl or Br) are stable for days in concentrated acid such as $HClO_4$ or the corresponding hydrohalogenic acid HX. However, when $[M(cp)_2X_2]^+$ was dissolved in HX′ (X′ = Br or Cl respectively) exchange occurred, more rapidly for X = Br and X′ = Cl than for X = Cl and X′ = Br, and the initial e.s.r. spectrum changed to that of $[M(cp)_2X'_2]^+$ in all cases. For M = Mo or W there was a common intermediate spectrum comprising of four equal lines with a splitting similar to $\langle a \rangle$ (Br) for $[M(cp)_2Br_2]^+$, and when M = Mo satellites due to ^{95}Mo–^{97}Mo were distinguishable. These intermediates must be the mixed halide cations containing one interacting Br ligand [equation (2)]. This was confirmed for M = Mo by synthesis and isolation of the $[PF_6]^-$ salt in the sequence (3) (*cf.* ref. 12 for the first step).

$$[M(cp)_2Cl_2]^+ \underset{HCl}{\overset{HBr}{\rightleftharpoons}} [M(cp)_2(Br)Cl]^+ \underset{HCl}{\overset{HBr}{\rightleftharpoons}} [M(cp)_2Br_2]^+ \qquad (2)$$

$$[Mo(cp)_2(SMe)_2] \xrightarrow[(ii)\ [H_4N][PF_6]]{(i)\ MeBr} [Mo(cp)_2Br(SMe_2)][PF_6] \xrightarrow[dme]{LiCl} [Mo(cp)_2(Br)Cl] \xrightarrow[(ii)\ [H_4N][PF_6]]{(i)\ oxidation} [Mo(cp)_2(Br)Cl][PF_6] \qquad (3)$$

DISCUSSION

Metal Hyperfine Coupling Constants.—Molybdenum-95 (15.8%) and ^{97}Mo (9.6%), both $I = \frac{5}{2}$, have similar coupling constants and give rise to overlapping sextets in solution so that only a mean value for $\langle a\rangle(\mathrm{Mo})$, the solution isotropic hyperfine coupling constant, can be determined. For $^{183}\mathrm{W}$ (14.3%), $I = \frac{1}{2}$, the satellites tend to be masked by the linewidth of the main $I = 0$ signal so that values for $\langle a\rangle(\mathrm{W})$ when obtainable are not as precise as those for Mo. Isotropic coupling arises primarily from direct or indirect unpaired *s*-electron density at the metal nucleus and in discussing this the contact term χ is more informative,[16,17] [equation (4)], where $\langle a\rangle = -K + (\langle g\rangle - 2.0023)P$ and

$$\chi = -\tfrac{3}{2}\left(\frac{hca_0^{3}}{2.0023\ \beta_e g_N \beta_N}\right)K \qquad (4)$$

$P = 2.0023\ \beta_e g_N \beta_N\ \langle r^{-3}\rangle$. Values of χ are listed in Tables 1 and 2. The negative sign is usually found for this term in transition-metal complexes and this has been assumed here, hence giving the sign of $\langle a\rangle(\mathrm{M})$. The value for $P(^{95}\mathrm{Mo}\text{–}^{97}\mathrm{Mo})$, -55×10^{-4} cm^{-1}, was based on that of McGarvey [17] and P (^{183}W) was estimated as $+50 \times 10^{-4}$ cm^{-1}, but a wide variation in these values has little effect on χ.

For Mo, χ lies in the narrow range -3.9 to -4.5 atomic units (a.u.) for all cations except those with toluene-3,4-dithiolate (tdt). The values are more positive than those found for molybdenyl compounds but similar to that of $[\mathrm{Mo(CN)_8}]^{3-}$ (-3.91 a.u.).[17,18] This may be explained by a little direct 5*s* contribution to the ground state, since the orbital has the A_1 symmetry of the ground state of a C_{2v} species {see below, $[\mathrm{M(cp)_2(X)Y}]^+$ (X = Y)}, the highest symmetry possible in these cations. However, as the theoretical contact term for $5s^1$ is *ca.* +250 a.u.[19] the *s* character can be no more than 1—2%. The positive shift of χ may also partially arise from delocalisation of the electron from the metal on to the ligands.

The spectra of glasses of $[\mathrm{Mo(cp)_2X_2}]^+$ (X = Cl or Br) are difficult to interpret but contain metal hyperfine couplings. For $[\mathrm{Mo(cp)_2Cl_2}]$ the largest coupling constant $T_1(\mathrm{Mo})$ was $(50 \pm 2) \times 10^{-4}$ cm^{-1} giving one principal value of the anisotropic coupling constant as $A_{1(\mathrm{aniso.})}$ (Mo) $= +15.5 \times 10^{-4}$ cm^{-1}. The other two values are obscured by the linewidths of the $I = 0$ peaks so further analysis is impossible.

The χ value for $[\mathrm{Mo(cp)_2(tdt)}]^+$ is more positive than for other cations. This must reflect the nature of the dithiolate ligand and probably arises from a ground state molecular orbital that contains a greater contribution from ligand orbitals, S(3*p*). For cations $[\mathrm{W(cp)_2(X)Y}]^+$, χ is fairly constant (-9 to -11 a.u.) and is similar to that for $[\mathrm{W(CN)_8}]^{3-}$.[17,18] Reported e.s.r. data for other tungsten (d^1) species [16] give more negative values of χ and the difference may be explained as for molybdenum cations. Cations containing S-bound ligands have more positive values of χ and again this may indicate more ligand character in the ground state.

Ligand Hyperfine Coupling Constants.—Only in the cases of halogeno-compounds are well defined isotropic couplings to the X and Y ligands observed, although there is evidence for a poorly resolved ^{14}N coupling ($<4.5 \times 10^{-4}$ cm^{-1}) in the spectrum of $[\mathrm{Mo(cp)_2(NHC_6H_4O)}]^+$. Hyperfine structure due to ^{35}Cl and ^{37}Cl, $I = \frac{3}{2}$, are indistinguishable so that a mean value of $\langle a\rangle(\mathrm{Cl})$, primarily due to ^{35}Cl, is obtained. For $[\mathrm{W(cp)_2Cl_2}]^+$, $\langle a\rangle(\mathrm{Cl})$ is obscured by the linewidth but must be $<5 \times 10^{-4}$ cm^{-1}. For $[\mathrm{Mo(cp)_2Cl_2}]^+$, $\langle a\rangle$ (Cl) represents an *s*-electron density at each ^{35}Cl of *ca.* 0.2% but this density is higher for the compounds $[\mathrm{M(cp)(C_6F_5)(\eta\text{-}C_5H_4{\cdot}C_6F_5)Cl}]^+$ (M = Mo or W) which have a substituted η-$\mathrm{C_5H_5}$ group and a metal–fluorocarbon bond.

The cations $[\mathrm{Mo(cp)_2(X)Y}]^+$ (X = Y = Br; X = Cl, Y = Br) also both have *s*-electron densities on ^{79}Br–^{81}Br of *ca.* 0.2% so that the ground-state molecular orbitals of all the simple halogenomolybdenum compounds must have a similar ligand contribution. For $[\mathrm{W(cp)_2(X)Y}]^+$ (X = Y = Br; X = Cl, Y = Br), $\langle a\rangle(\mathrm{Br})$ values are also similar but greater than for the molybdenum analogues and this latter fact may be due to greater delocalisation on to the ligand, although more indirect spin polarisation by unpaired spin in tungsten *d* orbitals may cause this difference. The cation $[\mathrm{W(cp)(C_6F_5)(\eta\text{-}C_5H_4{\cdot}C_6F_5)Br}]^+$, like the corresponding chloro-cation, shows the largest $\langle a\rangle(\mathrm{X})$ value (*ca.* 0.4% *s* character).

The ground-state molecular orbital for these cations, which in the most symmetrical cases have a C_{2v} point group, has been shown by various calculations to be of A_1 symmetry.[3,4,6–8] The relevant metal orbitals are $d_{x^2-y^2}$, d_{z^2}, *s*, and p_z but χ values rule out much *s* character in the highest-occupied ground-state orbital ($\psi_{\mathrm{homo.}}$) and p_z similarly is probably unimportant so that the metal contribution is mainly ψ_{M}. The *p* orbitals of X in

$$\psi_{\mathrm{M}} = a(d_{x^2-y^2}) + b(d_{z^2}) \qquad (5)$$

$[\mathrm{M(cp)_2X_2}]$ in the *zx* plane will combine to form a ligand π-group orbital of A_1 symmetry (Figure 1). The ligand

$$\psi_{\mathrm{X}(\pi)} = 2^{-\frac{1}{2}}(p_{x_1} - p_{x_2}) \qquad (6)$$

$A_1(\sigma)$ orbital, $2^{-\frac{1}{2}}(p_{z_1} + p_{z_2})$, will have poor overlap with the *d* orbitals and may be neglected. Also group orbitals from cp ligands may be involved but their contribution to $\psi_{\mathrm{homo.}}$ may be considered constant in this series of cations. Hence direct delocalisation of unpaired electron density on to the X ligands may occur

$$\psi_{\mathrm{homo.}} = \alpha\psi_{\mathrm{M}} + \beta\psi_{\mathrm{X}(\pi)} + [(\mathrm{cp})_2 \text{ contributions and smaller terms}] \qquad (7)$$

and spin polarisation of inner *s* orbitals by $\psi_{\mathrm{X}(\pi)}$ will give rise to $\langle a\rangle(\mathrm{X})$. Thus $\langle a\rangle(\mathrm{X})$ may be related to π bonding but it is impossible to rule out a contribution from some spin polarisation of M–X σ bonds by ψ_{M}. Anisotropic coupling parameters, $A_{\mathrm{aniso.}}$ (X), would be more informative but although spectra of glasses of

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[16] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 155.

[17] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.

[18] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, 1964, **86**, 2799.

[19] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, 1967.

$[M(cp)_2Br_2]^+$ show splitting due to ^{79}Br—^{81}Br the analysis is complicated by non-coincidence of g and T tensors and is still under investigation.

g *Values*.—The isotropic $\langle g \rangle$ values listed in Tables 1 and 2 show a general increase for both molybdenum and tungsten species and correspond roughly to a change through the order of co-ordinated atoms O, N, Cl, S, and Br of the ligands X and Y. Solvent effects on these values are small as shown, and, for example for $[W(cp)_2Cl_2]^+$ varied $< \pm 0.001$ in 1,2-dimethoxyethane, dichloromethane, acetone, dimethyl sulphoxide, or concentrated hydrochloric acid.

Since the $\langle g \rangle$ values are very ligand dependent they may be used in relation to the structures of the cations in a similar way to that of chemical shifts in n.m.r. spectroscopy. Thus, the mixed cations $[M(cp)_2(Br)Cl]^+$ (M = Mo or W) or $[W(cp)_2Cl(NCS)]^+$ have $\langle g \rangle$ values at the mean of those of $[M(cp)_2Cl_2]^+$ and $[M(cp)_2Br_2]^+$ or $[W(cp)_2(NCS)_2]^+$ respectively (within experimental error). Also the structure of $[W(cp)_2(NCS)(SCN)]$ determined by other means [15] is supported by the fact that the cation formed on oxidation has a $\langle g \rangle$ value higher than $[W(cp)_2(NCS)_2]^+$ and closer to other cations with S-bonded ligands.

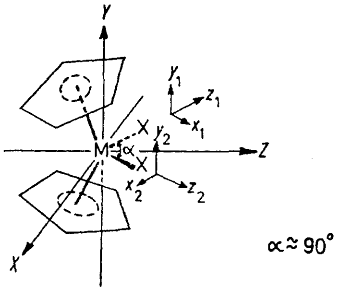

FIGURE 1 Geometry and co-ordinate systems used for $[M(cp)_2X_2]^+$

The variation $\Delta g = \langle g \rangle - 2.0023$ arises from mixing of the A_1 (for C_{2v} symmetry) ground state with excited states and since Δg is either positive or negative both filled and unfilled orbitals must be involved. A generalisation of the expression obtained from perturbation theory for spin-orbit coupling is (8),[19,20] where ξ_M

$$\Delta g = \tfrac{1}{3}\sum_i[\xi_M(A_i) + \xi_{lig}(B_i)]/\Delta E_i \qquad (8)$$

is the metal spin-orbit coupling constant and ξ_{lig} represents a linear function of the spin-orbit coupling constants of the ligand atoms; A and B are factors obtained from the LCAO molecular orbitals of the ground-state ($\psi_{homo.}$) and excited states (ψ_i) of energy difference ΔE_i. The coupling ξ_M will be essentially constant in these cations for a given metal ($\xi_W > \xi_{Mo}$). There should be little change in A_i or B_i for these cations of the same geometry, especially when χ and $\langle a \rangle$(X) (X = Cl or Br) reflect similar contact interactions at metal and ligand for Mo or W. Values of ΔE_i for observed electronic transitions have been reported for some $[M(cp)_2X_2]^+$ and $[M(cp)_2(X)Y]$ compounds and, although assignments are uncertain, there is not a great variation in ΔE_i with change of X or Y.[10] Thus the main factor to be considered on changing X or Y is ξ_{lig}, in particular the spin-orbit coupling constants of X and Y ligands since the $M(cp)_2$ system is unchanged. The relation of Δg to the sum $(\xi_X + \xi_Y)$, where X and Y may be equivalent, is shown in Figure 2 and for both Mo and W there is almost a linear relation for many cations. The main exceptions contain S-bound ligands and these probably reflect major differences in the A and B terms (*cf.* χ values).

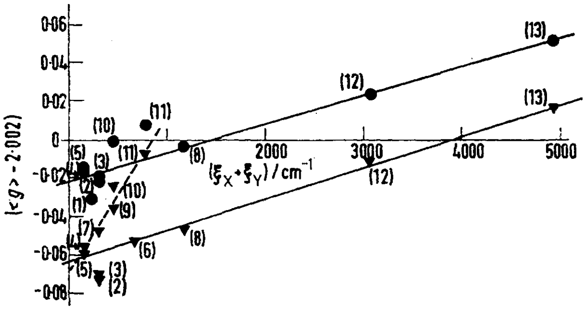

FIGURE 2 Relation of $(\langle g \rangle - 2.002)$ to $(\xi_X + \xi_Y)$ for $[Mo(cp)_2(X)Y]^+$ (●) and $[W(cp)_2(X)Y]^+$ (▼): XY = HNC_6H_4O (1), $(O_2CCF_3)_2$ (2), $(O_2CPh)_2$ (3), $(NCS)_2$ (4), $(N_3)_2$ (5), Cl(NCS) (6), $O_2C_{14}H_8$ (7), Cl_2 (8), (NCS)(SCN) (9), HNC_6H_4S (10), tdt (11), Br(Cl) (12), and Br_2 (13)

Spectra from frozen solutions of $[M(cp)_2X_2]^+$ (M = Mo or W; X = Cl or Br) give the principal values of the g tensor shown in Table 3. The values in parentheses were obtained using $g_1 + g_2 + g_3 = 3\ \langle g \rangle$ but are experimentally supported. For M = Mo and X = Br, g_2 and g_3 cannot be precisely determined but both lie within 2.03 ± 0.02. The assignment of principal values of the g tensor from spectra of glasses is not straightforward but in all cases two of the g values (g_2 and g_3)

TABLE 3

E.s.r. parameters from frozen solutions

Cation	g_1 [a]	g_2 [a]	g_3 [a]
$[Mo(cp)_2Cl_2]^+$	1.984	(1.997) [b]	2.015
$[Mo(cp)_2Br_2]^+$	2.101	See text	
$[W(cp)_2Cl_2]^+$	1.903	(1.967) [b]	1.991
$[W(cp)_2Br_2]^+$	2.054	1.992	(1.996) [b]
$[W(cp)_2Cl(NCS)]^+$	1.879	(1.972) [b]	1.995

[a] Principal values of the g tensor (±0.003). [b] Calculated using $g_1 + g_2 + g_3 = 3\langle g \rangle$.

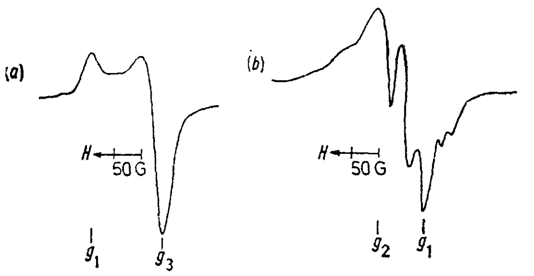

FIGURE 3 E.s.r. spectra of $[W(cp)_2Cl_2]^+$ (*a*) and $[W(cp)_2Br_2]^+$ (*b*) in frozen dimethyl sulphoxide solution

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[20] A. J. Stone, *Proc. Roy. Soc.*, 1963, **A271**, 424.

lie close together and approach 2. These values may tentatively be assigned to g_z and g_x. On the other hand g_1 varies markedly and if this is assigned to g_y this would reflect the influence of the MX_2 (MXY) system, since the excited states determining g_y are of B_1 symmetry and these include the metal d_{zx} orbital and group orbital $2^{-\frac{1}{2}}$ $(p_{z_1} - p_{z_2})$ from X_2 ligands which will give rise to strong M–X σ and σ^* interactions, the former involving much ligand character. Mixing of B_1 (σ) with the ground state would cause a positive shift in g_y with increasing ξ_X and the main variation in $\langle g \rangle$ may be caused by this variation in g_1.

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